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In the matter of an application for a German Patent in the name of Merck Patent GmbH, filed under No. 101 09 032.3 on 24 February 2001, and in the matter of an application for a U.S. Patent.

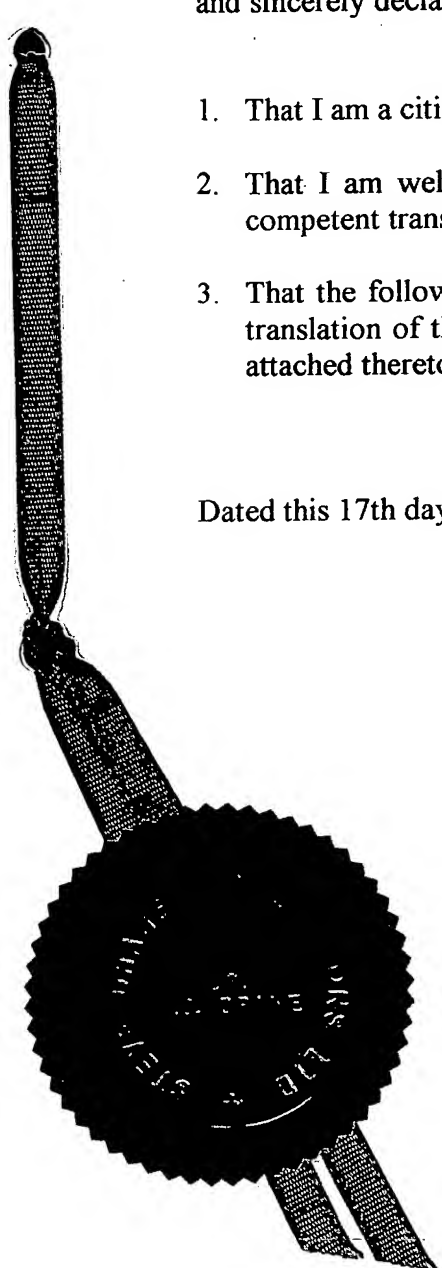
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1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That I am well acquainted with the German and English languages and am a competent translator thereof.
3. That the following is to the best of my knowledge and belief a true and correct translation of the above-referenced patent application and the Official Certificate attached thereto

Dated this 17th day of September 2004



Dr. Ashwood Stephen Drane



# FEDERAL REPUBLIC OF GERMANY

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## Priority certificate regarding the filing of a patent application

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**Applicant/proprietor:** Merck Patent Gesellschaft mit beschränkter Haftung,  
Darmstadt/DE

**Title:** Fluoroalkylphosphate salts, and process for the  
preparation of these substances

**IPC:** C 07 F, C 07 D, C 08 K

The attached pages are a correct and accurate reproduction of the original  
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Munich, 7 November 2001  
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**mit beschränkter Haftung**  
**64271 Darmstadt**

**Fluoroalkylphosphate salts, and process for the**  
**preparation of these substances**

## **Fluoroalkylphosphate salts, and process for the preparation of these substances**

5 The present invention relates to fluoroalkylphosphate salts and to a process for their preparation. The present invention furthermore relates to mixtures which comprise the fluoroalkylphosphate salts according to the invention, and to the use of these salts or these mixtures in electrolytes, primary batteries, secondary batteries, capacitors, supercapacitors or galvanic cells.

10

The spread of portable electronic equipment, such as, for example, laptop and palmtop computers, mobile telephones or video cameras, and thus also the demand for lightweight and high-performance batteries, has increased dramatically worldwide in recent years.

15

In view of this suddenly increased demand for batteries and the associated ecological problems, the development of rechargeable batteries with a long service life is of constantly increasing importance.

20 Rechargeable lithium ion batteries have been commercially available since the early nineties. Most of these batteries work with lithium hexafluorophosphate as conductive salt. However, this lithium salt is an extremely hydrolysis-sensitive compound with low thermal stability, and consequently the corresponding lithium batteries, owing to these properties of the salt, can only be produced by  
25 very complex and thus also very expensive processes.

In addition, the sensitivity reduces the service life and the performance of these lithium batteries and also impairs their use under extreme conditions, such as, for example, high temperatures.

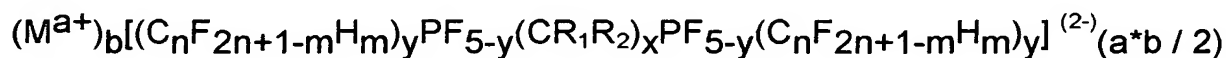
For these reasons, lithium perfluoroalkylfluorophosphates, which have better  
30 chemical and electrochemical stabilities and high discharge efficiency compared with conventional  $\text{LiPF}_6$ , have been developed for lithium batteries as

conductive salts in electrolytes of high-energy lithium batteries. The high hydrolysis stability of lithium perfluoroalkylfluorophosphates makes them interesting as powerful lithium batteries in electric vehicles (M. Schmidt, U. Heider, A. Kühner, R. Oesten, M. Jungnitz, N. Ignat'ev, P. Sartori. J. of Power Sources (accepted), WO 98/15562 (Merck KgaA), P 100 08 955.0 (Merck KgaA), N. Ignat'ev and P. Sartori, J. of Fluorine Chem., 101 (2000), p. 203-207).

The disadvantage of these substances lies in their high molecular weight and the resultant low content of  $\text{Li}^+$  cations per weight unit of conductive salt.

- 10 The object of the present invention was therefore to provide stable conductive salts having a higher content of cations per weight unit of conductive salt. A further object of the invention was also to extend or improve the service life and the performance of primary and secondary batteries, capacitors, super-capacitors and/or galvanic cells.

15 This object is achieved by the provision of novel fluoroalkylphosphate salts of the general formula (I)



20

(I)

in which

$\text{M}^{a+}$  a monovalent, divalent or trivalent cation,

25

$a = 1, 2 \text{ or } 3,$

$b = 2 \text{ for } a = 1,$

$b = 2 \text{ for } a = 3,$

30

$b = 1 \text{ for } a = 2$

and in each case

$$1 \leq n \leq 8,$$

5  $0 \leq m \leq 2$  for  $n = 1$  or  $2$ ,

$$0 \leq m \leq 4$$
 for  $3 \leq n \leq 8$ ,

$$1 \leq x \leq 12,$$

10  $0 \leq y \leq 2,$

where  $R_1$  and  $R_2$  are identical or different and are selected from the group consisting of fluorine, hydrogen, alkyl, fluoroalkyl and perfluoroalkyl substituents, and

15 where the substituents ( $C_nF_{2n+1-m}H_m$ ) are in each case identical or different.

Preference is given to fluoroalkylphosphate salts of the general formula (I)  
20 according to the invention in which the cation  $M^{a+}$  is an alkali metal cation, preferably a lithium, sodium or potassium cation, particularly preferably a lithium cation, a magnesium or aluminium cation.

Preference is furthermore also given to fluoroalkylphosphate salts of the general formula (I) in which the cation  $M^{a+}$  is an organic cation, preferably  
25

a nitrosyl cation, a nitril cation or a cation of the general formula  $[N(R^7)_4]^+$ ,  $[P(R^7)_4]^+$ ,  $[P(N(R^7)_2)_4]^+$  or  $[C(N(R^7)_2)_3]^+$ , where the radicals  $R^7$  are in each case identical or different and stand for

30

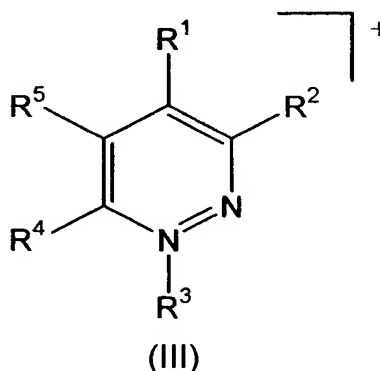
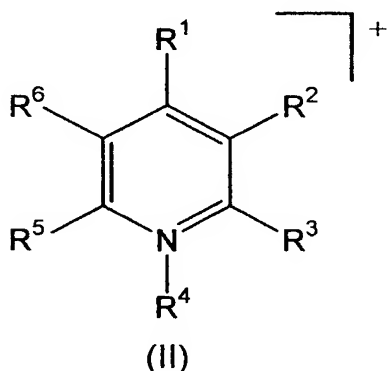
H or alkyl ( $C_{1-10}$ ),

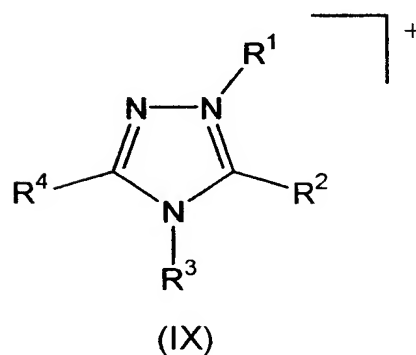
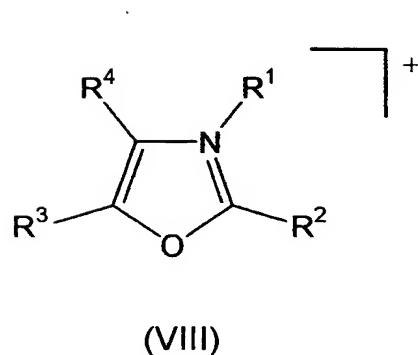
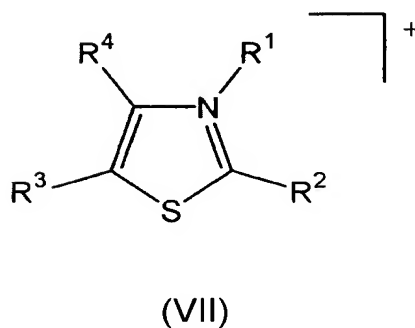
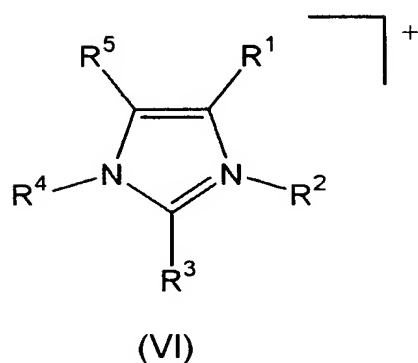
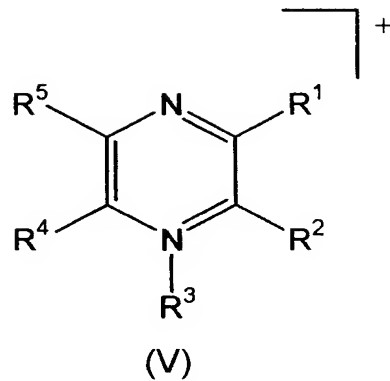
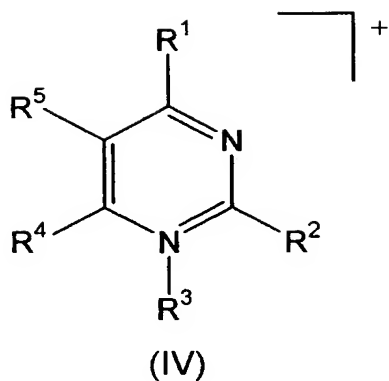
where any H atoms in the alkyl chain may be substituted by fluorine or an aromatic radical, optionally containing heteroatoms, or a cycloalkyl radical, preferably having 5-6 members, and/or C atoms in the alkyl chain may be replaced by heteroatoms, preferably oxygen.

The aromatic or cycloaliphatic radical A employed, which may optionally contain heteroatoms, may be any aromatic, heteroaromatic or cycloaliphatic radicals known to the person skilled in the art and suitable for the preparation of  $[N(R^7)_4]^+$ ,  $[P(R^7)_4]^+$ ,  $[P(N(R^7)_2)_4]^+$  or  $[C(N(R^7)_2)_3]^+$  cations.

A is preferably in each case a 5- or 6-membered aromatic radical, optionally containing nitrogen and/or sulfur and/or oxygen atoms, or a cycloalkyl radical, preferably having 5 or 6 members, particularly preferably a phenyl or pyridine radical.

In a further preferred embodiment of the present invention, the cation  $M^{a+}$  is a heteroaromatic cation selected from the group consisting of the heteroaromatic cations of the general formula (II) to (IX):





- 5 The radicals  $R^1$  to  $R^6$ , which may in each case be identical or different, are an H radical, a halogen radical, preferably a fluorine radical, or a  $C_{1-8}$ -alkyl radical, which may optionally be substituted by the substituents F, Cl,  $N(C_rF_{(2r+1-s)}H_s)_2$ ,  $O(C_rF_{(2r-1-s)}H_s)$ ,  $SO_2(C_rF_{(2r+1-s)}H_s)$  or  $C_rF_{(2r+1-s)}H_s$ , in which  $1 \leq r \leq 6$  and  $0 \leq s \leq 13$ .



It is also possible for two of the radicals  $R^1$  to  $R^6$  together to be a  $C_{1-8}$ -alkyl radical, which may optionally be substituted by the substituents F, Cl,  $N(C_rF_{(2r+1-s)}H_s)_2$ ,  $O(C_rF_{(2r+1-s)}H_s)$ ,  $SO_2(C_rF_{(2r+1-s)}H_s)$  or  $C_rF_{(2r+1-s)}H_s$ , in which  $1 \leq r \leq 6$  and  $0 \leq s \leq 2r+1$ .

- 5 It should be noted that the radicals  $R^1$  to  $R^6$  in the heteroaromatic cations of the general formula (II) to (IX) cannot be halogens if the radicals  $R^1$  to  $R^6$  are bonded directly to nitrogen.

10 Preference is likewise given to fluoroalkylphosphate salts of the general formula (I) in which  $1 \leq n \leq 6$ , preferably  $1 \leq n \leq 3$ .

Preference is also given to fluoroalkylphosphate salts of the general formula (I) in which  $1 \leq x \leq 8$ , preferably  $1 \leq x \leq 4$ .

- 15 Particular preference is given to fluoroalkylphosphate salts of the general formula (I) in which  $m = 0$ .

Very particular preference is given to fluoroalkylphosphate salts of the general formula (I) in which  $y = 2$ .

- 20 Very particular preference is also given to the fluoroalkylphosphate salts of the general formula (I) according to the invention in which  $R_1$  and  $R_2$  are = fluorine.

- 25 Particular preference is given to the fluoroalkylphosphate salts of the general formula (I):



and



The salts of the general formula (I) according to the invention can be employed, both in pure form and in the form of their mixtures, as conductive salts in electrolytes, primary and secondary batteries, capacitors, super-capacitors and/or galvanic cells. The salts according to the invention are preferably used in pure form as conductive salts since in this way particularly good reproducibility of the electrochemical properties can be ensured.

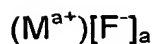
However, it is likewise possible to use the salts according to the invention as conductive salts in the form of a mixture with further salts known to the person skilled in the art.

They can be used in proportions of between 1 and 99% in combination with other conductive salts used in electrochemical cells. Suitable are, for example, conductive salts selected from the group consisting of  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$ ,  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$  or lithium fluoroalkylphosphates of the general formula  $\text{Li}[\text{PF}_{(6-c)}(\text{C}_d\text{F}_{2d+1})]$ , where  $1 \leq c \leq 5$  and  $1 \leq d \leq 8$ , and  $\text{LiN}[\text{SO}_2(\text{C}_e\text{F}_{2e+1})]_2$ ,  $\text{LiCSO}_2(\text{C}_e\text{F}_{2e+1})_3$  and  $\text{Li}[\text{SO}_3(\text{C}_e\text{F}_{2e+1})]$ , where  $2 \leq e \leq 8$ , and mixtures thereof.

The salts of the formula (I) and mixtures thereof can likewise be used in electrolytes for electrochemical cells.

The electrolytes may also comprise organic isocyanates (DE 199 44 603, where this citation is hereby incorporated by way of reference and is thus regarded as part of the disclosure) in order to reduce the water content.

The invention furthermore relates to a process for the preparation of fluoroalkylphosphate salts according to the invention. In this process, at least one  $\alpha,\omega$ -bis[fluoro(fluoroalkyl)fluorophosphorano]fluoroalkane is reacted with at least one fluoride salt of the general formula (X)



(X)

in which ( $M^{a+}$ ) and  $a$  are as defined above, in solution to give a fluoroalkyl-phosphate salt of the general formula (I) according to the invention, and the latter is, where appropriate, purified and/or isolated by conventional methods.

In a preferred embodiment of the process according to the invention, the  $\alpha,\omega$ -bis[fluoro(fluoroalkyl)fluorophosphorano]fluoroalkanes employed are at least one compound of the general formula (XI)



(XI)

in which

$$1 \leq n \leq 8, 0 \leq m \leq 2 \text{ for } n = 1 \text{ or } 2, 0 \leq m \leq 4 \text{ for } 3 \leq n \leq 8, 1 \leq x \leq 12, \\ 0 \leq y \leq 2,$$

where  $R_1$  and  $R_2$  are identical or different and are selected from the group consisting of fluorine, hydrogen, alkyl, fluoroalkyl and perfluoroalkyl substituents, and

where the substituents ( $C_nF_{2n+1-m}H_m$ ) are in each case identical or different.

Of the processes according to the invention, preference is given to those in which the compound of the general formula (X) is employed in an excess of up to 10 fold, preferably up to 5 fold, particularly preferably up to 2 fold, based on the amount of fluoro- $\alpha,\omega$ -bis(alkylfluorophosphorano)alkane(s).

Compounds of the general formula (X) are very particularly preferably employed in twice the equimolar amount based on the (fluoro- $\alpha,\omega$ -alkane-diyl)bis[fluoro(fluoroalkyl)]phosphorane employed.

- 5 In the processes according to the invention, the reaction with the fluoride salt of the general formula (X) is preferably carried out at a temperature of from -35 to +80°C, preferably from -20 to +50°C, particularly preferably from 10 to 25°C.

Suitable solvents for the above-mentioned processes are organic carbonates, preferably ethylene carbonate, propylene carbonate, butylene carbonate, di-  
10 methyl carbonate, diethyl carbonate, ethyl methyl carbonate or methyl propyl carbonate, organic esters, preferably methyl formate, ethyl formate, methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, methyl butyrate, ethyl butyrate,  $\gamma$ -butyrolactone, organic ethers, preferably diethyl ether, di-  
15 methoxyethane or diethoxyethane, organic amides, preferably dimethylformamide, dimethylacetamide, sulfur-containing solvents, preferably dimethyl sulfoxide, dimethyl sulfide, diethyl sulfide or propane sulfone, aprotic solvents, preferably acetonitrile, acrylonitrile, propionitrile or acetone, or at least partially fluorinated derivatives of the above-mentioned solvents, or mixtures of at least  
20 two of these solvents and/or fluorinated derivatives of these solvents.

The fluoroalkylphosphate salts of the general formula (I) according to the invention are also suitable for use in solid electrolytes. For the purposes of the invention, the term solid electrolytes is taken to mean both polymer electro-  
25 lytes, which usually comprise an optionally crosslinked polymer and a conductive salt, and also gel electrolytes, which, besides an optionally crosslinked polymer and a conductive salt, usually additionally comprise at least one solvent.

30 The present invention therefore furthermore also relates to a mixture comprising

a) at least one fluoroalkylphosphate salt of the general formula (I)

and

5

b) at least one polymer.

For the purposes of the present invention, the term mixture covers pure mix-  
tures of components a) and b), mixtures in which the salt of component a) is  
10 included in the polymer of component b), and mixtures in which chemical  
and/or physical bonds exist between the salt of component a) and the polymer  
of component b).

In a preferred embodiment of the present invention, the mixture according to  
15 the invention comprises from 5 to 90% by weight of component a) and from 95  
to 5% by weight of component b), particularly preferably from 10 to 80% by  
weight of component a) and from 90 to 20% by weight of component b). The  
stated weight ratios are in each case based on the sum of components a) and  
b).

20

As component b), the mixture according to the invention preferably comprises  
a homopolymer or copolymer of acrylonitrile, vinylidene difluoride, methyl  
(meth)acrylate, tetrahydrofuran, ethylene oxide, siloxane, phosphazene or a  
mixture of at least two of the above-mentioned homopolymers and/or copoly-  
25 mers.

30

Component b) is particularly preferably a homopolymer or copolymer of vinyli-  
dene difluoride, acrylonitrile, methyl (meth)acrylate or tetrahydrofuran, very  
particularly preferably a homopolymer or copolymer of vinylidene difluoride.

These homopolymers and copolymers of vinylidene difluoride are marketed under the name Kynar<sup>®</sup> and Kynarfex<sup>®</sup> by Atofina Chemicals, Inc., and under the name Solef<sup>®</sup> by Solvay.

- 5 The polymers used in accordance with the invention may also be at least partially crosslinked. The crosslinking can be carried out using known crosslinking agents by conventional methods known to the person skilled in the art.

10 Besides the fluoroalkylphosphate salts of the general formula (I) and the polymers, the mixture according to the invention may additionally comprise a solvent or a solvent mixture of two or more solvents.

Preferred solvents are organic carbonates, preferably ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, 15 ethyl methyl carbonate or methyl propyl carbonate, organic esters, preferably methyl formate, ethyl formate, methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, methyl butyrate, ethyl butyrate,  $\gamma$ -butyrolactone, organic ethers, preferably diethyl ether, dimethoxyethane, diethoxyethane, organic amides, preferably dimethylformamide, dimethylacetamide, sulfur- 20 containing solvents, preferably dimethyl sulfoxide, dimethyl sulfide, diethyl sulfide or propane sulfone, aprotic solvents, preferably acetonitrile, acrylonitrile or acetone, or at least partially fluorinated derivatives of the above-mentioned solvents, or mixtures of at least two of these solvents and/or fluorinated derivatives of these solvents.

25 The present invention furthermore relates to the use of at least one fluoroalkylphosphate salt according to the invention or a mixture according to the invention in electrolytes, primary batteries, secondary batteries, capacitors, supercapacitors and/or galvanic cells, if desired also in combination with further, 30 known conductive salts and/or additives.

The invention furthermore relates to electrolytes, primary and secondary batteries, capacitors, supercapacitors and galvanic cells which contain at least one fluoroalkylphosphate salt of the general formula (I) according to the invention or a mixture according to the invention and, if desired, further conductive salts and/or additives. Further conductive salts and additives are known to the person skilled in the art, for example from Doron Auerbach, Nonaqueous Electrochemistry, Marc Dekker Inc., New York 1999; D.Linden, Handbook of Batteries, Second Edition, McGraw-Hill Inc., New York 1995, and G. Maman-  
10 VCH Verlagsgesellschaft, Weinheim 1994. They are hereby incorporated by way of reference and are regarded as part of the disclosure.

Electrolytes according to the invention preferably have a concentration of the fluoroalkylphosphate salt(s) according to the invention of from 0.01 to 3 mol/l, preferably from 0.01 to 2 mol/l, particularly preferably from 0.1 to 1.5 mol/l.  
15

As solvents for the salts according to the invention, the electrolytes preferably comprise organic carbonates, preferably ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate or methyl propyl carbonate, organic esters, preferably methyl formate, ethyl formate, methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, methyl butyrate, ethyl butyrate,  $\gamma$ -butyrolactone, organic ethers, preferably diethyl ether, dimethoxyethane, diethoxyethane, organic amides, preferably dimethylformamide, dimethylacetamide, sulfur-containing solvents, preferably dimethyl sulfoxide, dimethyl sulfide, diethyl sulfide or propane sulfone, aprotic solvents, preferably acetonitrile, acrylonitrile or acetone, or at least partially fluorinated derivatives of the above-mentioned solvents, or mixtures of at least two of these solvents and/or fluorinated derivatives of these solvents.  
25  
30

The fluoroalkylphosphate salts according to the invention and the mixtures according to the invention have the advantage that they exhibit absolutely no or virtually no signs of decomposition over a very long period in the presence of water and have good to very good solubility in most solvents or solvent mixtures.

Furthermore, they have high thermal stability and high chemical stability both in the solid state and in the dissolved state. Thus, the salts and mixtures according to the invention are stable, for example to strong oxidants, such as, for example, to highly oxidising electrode materials, such as, for example,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$  or  $\text{LiCoO}_2$ .

These properties enable electrolytes, batteries, capacitors, supercapacitors and galvanic cells which contain these conductive salts to be employed under extreme conditions, such as, for example, at high temperatures, without their service life and performance being impaired by these conditions.

Furthermore, the corresponding batteries, capacitors, supercapacitors and galvanic cells are distinguished by very good voltage constancy, unrestricted ability to function over many charging and discharging cycles, and by low production costs.

The use of the fluoroalkylphosphate salts according to the invention or the mixtures according to the invention in large batteries, as used, for example, in electric road vehicles or hybrid road vehicles, is likewise very advantageous since, in the case of damage to the batteries, such as, for example, in the case of an accident, including in the case of contact with water, for example through atmospheric moisture or extinguishing water, toxic and highly caustic hydrogen fluoride is not formed.

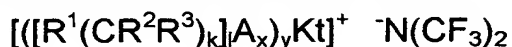


The compounds according to the invention and mixtures thereof can be used in electrolytes for electrochemical cells. They can be employed as conductive salts or additives. They can likewise be used in proportions of between 1 and 99% in combination with other conductive salts used in electrochemical cells.

- 5 Suitable are, for example, conductive salts selected from the group consisting of  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiN}(\text{CF}_3\text{CF}_2\text{SO}_2)_2$  and  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$  and mixtures thereof.

- 10 The electrolytes may also comprise organic isocyanates (DE 199 44 603) for reducing the water content.

It is also possible for compounds of the general formula



where

Kt denotes N, P, As, Sb, S, Se

- 15 A denotes N, P, P(O), O, S, S(O),  $\text{SO}_2$ , As, As(O), Sb, Sb(O)

$\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$

are identical or different

- and denote H, halogen, substituted and/or unsubstituted alkyl  $\text{C}_n\text{H}_{2n+1}$ , substituted and/or unsubstituted alkenyl having 1-18 carbon atoms and one or more double bonds, substituted and/or unsubstituted alkynyl having 1-18 carbon atoms and one or more triple bonds, substituted and/or unsubstituted cycloalkyl  $\text{C}_m\text{H}_{2m-1}$ , mono- or polysubstituted and/or unsubstituted phenyl, or substituted and/or unsubstituted heteroaryl,
- 20

A may be included in  $\text{R}^1$ ,  $\text{R}^2$  and/or  $\text{R}^3$  in various positions,

- 25 Kt may be included in a cyclic or heterocyclic ring,

the groups bonded to Kt may be identical or different

where

n denotes 1-18

m denotes 3-7

- 30 k denotes 0, 1-6

l denotes 1 or 2 in the case where  $x = 1$  and 1 in the case where  $x = 0$

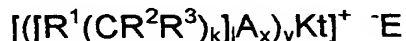
x denotes 0, 1

y denotes 1-4

to be present (DE 9941566). The process for the preparation of the compounds is characterised in that an alkali metal salt of the general formula



where  $D^+$  selected from the group consisting of the alkali metals, is reacted, in a polar organic solvent, with a salt of the general formula



where

10 Kt, A,  $R^1$ ,  $R^2$ ,  $R^3$ , k, l, x and y are as defined above, and

$^-E$  denotes  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $BF_4^-$ ,  $ClO_4^-$ ,  $AsF_6^-$ ,  $SbF_6^-$  or  $PF_6^-$ .

The compounds according to the invention may also be present in electrolytes comprising compounds of the formula



15 where

X denotes H, F, Cl,  $C_nF_{2n+1}$ ,  $C_nF_{2n-1}$ ,  $(SO_2)_kN(CR^1R^2R^3)_2$

Y denotes H, F or Cl

Z denotes H, F or Cl

$R^1$ ,  $R^2$ ,  $R^3$  denote H and/or alkyl, fluoroalkyl or cycloalkyl

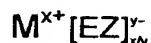
20 m denotes 0-9 and, if  $X = H$ ,  $m \neq 0$

n denotes 1-9

k denotes 0 if  $m = 0$  and  $k = 1$  if  $m = 1-9$ ,

prepared by reacting partially or perfluorinated alkylsulfonyl fluorides with dimethylamine in organic solvents (DE 199 466 73).

25 It is also possible to use electrolytes comprising complex salts of the general formula (DE 199 51 804)



in which:

x, y are 1, 2, 3, 4, 5 or 6

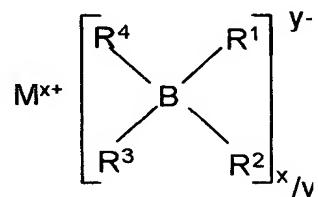
30  $M^{x+}$  is a metal ion

E is a Lewis acid selected from the group consisting of

$BR^1R^2R^3$ ,  $AlR^1R^2R^3$ ,  $PR^1R^2R^3R^4R^5$ ,  $AsR^1R^2R^3R^4R^5$ ,  $VR^1R^2R^3R^4R^5$ ,

$R^1$  to  $R^5$  are identical or different, are optionally bonded directly to one another by a single or double formation, and may each, individually or together, have the meaning of

- 5 a halogen (F, Cl or Br),  
an alkyl or alkoxy radical ( $C_1$  to  $C_8$ ), which may be partially or fully substituted by F, Cl, Br,  
an aromatic ring, optionally bonded via oxygen, from the group consisting of phenyl, naphthyl, anthracenyl, phenanthrenyl, which may be unsubstituted or
- 10 mono- to hexasubstituted by alkyl ( $C_1$  to  $C_8$ ) or F, Cl or Br,  
an aromatic heterocyclic ring, optionally bonded via oxygen, from the group consisting of pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or mono- to tetrasubstituted by alkyl ( $C_1$  to  $C_8$ ) or F, Cl or Br, and
- $Z$  is  $OR^6$ ,  $NR^6R^7$ ,  $CR^6R^7R^8$ ,  $OSO_2R^6$ ,  $N(SO_2R^6)(SO_2R^7)$ ,
- 15  $C(SO_2R^6)(SO_2R^7)(SO_2R^8)$ ,  $OCOR^6$ , where  
 $R^6$  to  $R^8$  are identical or different, are optionally bonded directly to one another by a single or double bond, and each, individually or together, have the meaning of
- a hydrogen or have the meaning as  $R^1$  to  $R^5$ , prepared by reacting a corre-
- 20 sponding boron or phosphorus Lewis acid/solvent adduct with a lithium or tetraalkylammonium imide, methanide or triflate.
- It is also possible for borate salts (DE 199 59 722) of the general formula



in which:

$M$  denotes a metal ion or tetraalkylammonium ion

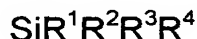
- 25  $x, y$  denote 1, 2, 3, 4, 5, 6,

R<sup>1</sup> to R<sup>4</sup> are identical or different and denote alkoxy or carboxyl radicals (C<sub>1</sub>-C<sub>8</sub>), which are optionally bonded directly to one another by a single or double bond,

to be present. These borate salts are prepared by reacting lithium tetraalkoxy-

5 borate or a 1:1 mixture of lithium alkoxide with a borate with a suitable hydroxyl or carboxyl compound in a ratio of 2:1 or 4:1 in an aprotic solvent.

Additives, such as silane compounds of the general formula



where R<sup>1</sup> to R<sup>4</sup> H

10 C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>

OC<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>

OC(O)C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>

OSO<sub>2</sub>C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>

and 1 ≤ x < 6

15 1 ≤ y ≤ 8 and

0 ≤ z ≤ 2y+1

and

R<sup>1</sup> – R<sup>4</sup> are identical or different

and are an aromatic ring from the group consisting of phenyl and naphthyl,

20 which may be unsubstituted or mono- or polysubstituted by F, C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>,

OC<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, OC(O)C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, OSO<sub>2</sub>C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, N(C<sub>n</sub>F<sub>2n+1-z</sub>H<sub>z</sub>)<sub>2</sub>, or

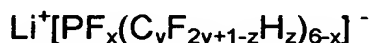
are a heterocyclic aromatic ring from the group consisting of pyridyl, pyrazyl

and pyrimidyl, each of which may be monosubstituted or polysubstituted by F,

C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, OC<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, OC(O)C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, OSO<sub>2</sub>C<sub>y</sub>F<sub>2y+1-z</sub>H<sub>z</sub>, N(C<sub>n</sub>F<sub>2n+1-z</sub>H<sub>z</sub>)<sub>2</sub>

25 (DE 100 276 26), may also be present.

The compounds according to the invention may also be employed in electrolytes comprising lithium fluoroalkylphosphates of the following formula



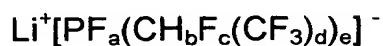
in which

30 1 ≤ x ≤ 5

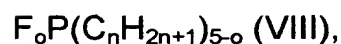
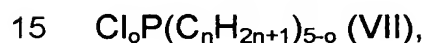
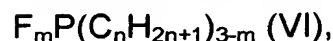
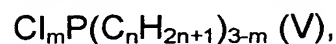
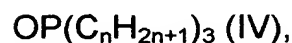
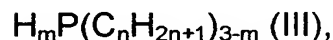
3 ≤ y ≤ 8

$$0 \leq z \leq 2y + 1$$

and the ligands ( $C_yF_{2y+1-z}H_z$ ) may be identical or different, with the exception of the compounds of the general formula



- 5 in which a denotes an integer from 2 to 5,  $b = 0$  or 1,  $c = 0$  or 1,  $d = 2$  and e denotes an integer from 1 to 4, with the provisos that b and c are not simultaneously each = 0, and the sum  $a + e$  is equal to 6, and the ligands ( $CH_bF_c(CF_3)_d$ ) may be identical or different (DE 100 089 55). The process for the preparation of lithium fluoroalkylphosphates is characterised in that at least
- 10 one compound of the general formula

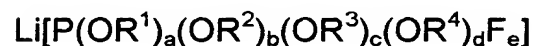


in each of which

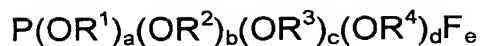
$$0 < m < 2, 3 < n < 8 \text{ and } 0 < o < 4,$$

- is fluorinated by electrolysis in hydrogen fluoride, the resultant mixture of fluorination products is separated by extraction, phase separation and/or distillation, and the resultant fluorinated alkylphosphorane is reacted with lithium fluoride in an aprotic solvent or solvent mixture with exclusion of moisture, and the resultant salt is purified and isolated by conventional methods.
- 20

- The compounds according to the invention may also be employed in electrolytes which comprise salts of the formula
- 25



- in which  $0 < a+b+c+d \leq 5$  and  $a+b+c+d+e = 6$ , and  $R^1$  to  $R^4$ , independently of one another, are alkyl, aryl or heteroaryl radicals, where at least two of  $R^1$  to  $R^4$  may be bonded directly to one another by a single or double bond (DE 100
- 30 16 801). The compounds are prepared by reacting phosphorus(V) compounds of the general formula



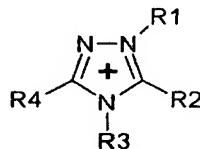
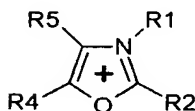
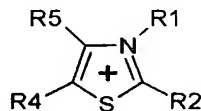
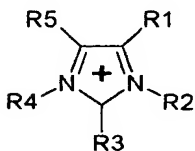
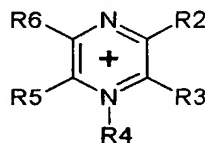
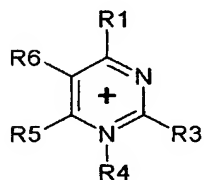
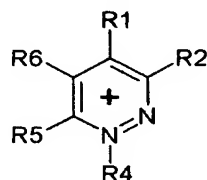
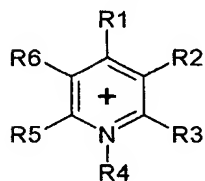
in which  $0 < a+b+c+d \leq 5$  and  $a+b+c+d+e = 5$ , and  $R^1$  to  $R^4$  are as defined above, with lithium fluoride in the presence of an organic solvent.

It is also possible for ionic liquids of the general formula



in which:

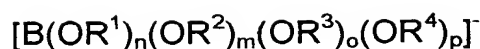
$K^+$  is a cation selected from the group consisting of



where  $R^1$  to  $R^5$  are identical or different, are optionally bonded directly to one another by a single or double bond, and each, individually or together, have the following meaning:

- H,
- halogen,
- an alkyl radical ( $C_1$  to  $C_8$ ), which may be partially or fully substituted by further groups, preferably F, Cl,  $N(C_nF_{(2n+1-x)}H_x)_2$ ,  $O(C_nF_{(2n+1-x)}H_x)$ ,  $SO_2(C_nF_{(2n+1-x)}H_x)$ ,  $C_nF_{(2n+1-x)}H_x$ , where  $1 < n < 6$  and  $0 < x \leq 13$ , and

$A^-$  an anion selected from the group consisting of



where  $0 \leq n, m, o, p \leq 4$ , and

$$m+n+o+p = 4$$

where  $R^1$  to  $R^4$  are different or are identical in pairs, are optionally bonded

5 directly to one another by a single or double bond and each, individually or together,

have the meaning of an aromatic ring from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or mono- or polysubstituted by  $C_nF_{(2n+1-x)}H_x$ , where  $1 < n < 6$  and  $0 < x \leq 13$ , or halogen or halogen (F, Cl, Br),

have the meaning of an aromatic heterocyclic ring from the group consisting of pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or mono- or polysubstituted by  $C_nF_{(2n+1-x)}H_x$ , where  $1 < n < 6$  and  $0 < x \leq 13$ , or halogen (F, Cl, Br),

15 have the meaning of an alkyl radical ( $C_1$  to  $C_8$ ), which may be partially or fully substituted by further groups, preferably F, Cl,  $N(C_nF_{(2n+1-x)}H_x)_2$ ,

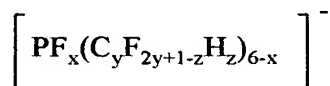
$O(C_nF_{(2n+1-x)}H_x)$ ,  $SO_2(C_nF_{(2n+1-x)}H_x)$ ,  $C_nF_{(2n+1-x)}H_x$ , where  $1 < n < 6$  and  $0 < x \leq 13$ , or  $OR^1$  to  $OR^4$ ,

individually or together, have the meaning of an aromatic or aliphatic carboxyl, dicarboxyl, oxysulfonyl or oxycarbonyl radical, which may be partially or fully

20 substituted by further groups, preferably F, Cl,  $N(C_nF_{(2n+1-x)}H_x)_2$ ,  $O(C_nF_{(2n+1-x)}H_x)$ ,  $SO_2(C_nF_{(2n+1-x)}H_x)$ ,  $C_nF_{(2n+1-x)}H_x$ , where  $1 < n < 6$  and  $0 < x \leq 13$  (DE 100 265 65), to be present in the electrolyte. It is also possible for ionic liquids  $K^+A^-$

where  $K^+$  is as defined above and

$A^-$  an anion selected from the group consisting of



25

and  $1 \leq x < 6$

$$1 \leq y \leq 8 \text{ and}$$

$$0 \leq z \leq 2y+1$$

to be present (DE 100 279 95).

The compounds according to the invention may also be present in electrolytes comprising compounds of the following formula:



in which

5  $R^1$  and  $R^2$  denote  $H$ ,  $C_yF_{2y+1-z}H_z$  or  $(C_nF_{2n-m}H_m)X$ , where  $X$  is an aromatic or heterocyclic radical, and

$R^3$  denotes  $(C_nF_{2n-m}H_m)Y$ , where  $Y$  is a heterocyclic radical, or  $(C_oF_{2o-p}H_p)Z$ , where  $Z$  is an aromatic radical,

and where  $n$ ,  $m$ ,  $o$ ,  $p$ ,  $y$  and  $z$  satisfy the following conditions:

10  $0 \leq n \leq 6$ ,

$0 \leq m \leq 2n$ ,

$2 \leq o \leq 6$ ,

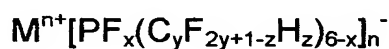
$0 \leq p \leq 2o$ ,

$1 \leq y \leq 8$ , and

15  $0 \leq z \leq 2y+1$ ,

for reducing the acid content in aprotic electrolyte systems in electrochemical cells.

It is also possible for fluoroalkylphosphates of the general formula



20 in which

$1 \leq x \leq 6$

$1 \leq y \leq 8$

$0 \leq z \leq 2y + 1$

$1 \leq n \leq 3$  and

25  $M^{n+}$  has the meaning of a mono- to trivalent cation, in particular:

$NR^1R^2R^3R^4$ ,

$PR^1R^2R^3R^4$ ,

$P(NR^1R^2)_kR^3_mR^4_{4-k-m}$  (where  $k=1-4$ ,  $m = 0-3$  and  $k+m \leq 4$ ),

$C(NR^1R^2)(NR^3R^4)(NR^5R^6)$ ,

30  $C(aryl)_3$ , Rb or tropylium,

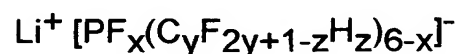


where  $R^1$  to  $R^8$  denote H, alkyl, aryl ( $C_1$ - $C_8$ ), which may be partially substituted by F, Cl or Br,

with the exception of  $M^{n+} = Li^+, Na^+, Cs^+, K^+$  and  $Ag^+$ , to be present. These fluoroalkylphosphates are obtainable by reacting phosphoranes with a fluoride or metal fluoroalkylphosphates with a fluoride or chloride in organic aprotic solvents (DE 100 388 58).

The electrolyte may also comprise a mixture which comprises

a) at least one lithium fluoroalkylphosphate salt of the general formula



in which

$$1 \leq x \leq 5$$

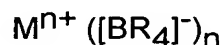
$$1 \leq y \leq 8 \text{ and}$$

$$0 \leq z \leq 2y+1$$

and the ligands  $(C_yF_{2y+1-z}H_z)$  are in each case identical or different and

b) at least one polymer (DE 100 58 264).

The electrolyte may also comprise tetrakisfluoroalkyl borate salts of the general formula



in which

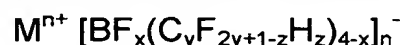
$M^{n+}$  is a monovalent, divalent or trivalent cation,

the ligands R are in each case identical and are  $(C_xF_{2x+1})$ , where  $1 \leq x \leq 8$ ,

and  $n = 1, 2$  or  $3$  (DE 100 558 11). The process for the preparation of tetrakisfluoroalkyl borate salts is characterised in that at least one compound of the general formula  $M^{n+} ([B(CN)_4]^-)_n$ , in which  $M^{n+}$  and  $n$  are as defined above,

is fluorinated by reaction with at least one fluorinating agent in at least one solvent, and the resultant fluorinated compound is purified and isolated by conventional methods.

The electrolyte may also comprise borate salts of the general formula



in which:

$1 < x < 3$ ,  $1 \leq y \leq 8$  and  $0 \leq z \leq 2y+1$  and

M denotes a mono- to trivalent cation ( $1 \leq n \leq 3$ ), apart from potassium and barium,

5 in particular:

Li,

$\text{NR}^1\text{R}^2\text{R}^3\text{R}^4$ ,  $\text{PR}^5\text{R}^6\text{R}^7\text{R}^8$ ,  $\text{P}(\text{NR}^5\text{R}^6)_k\text{R}^7_m\text{R}^8_{4-k-m}$  (where  $k=1-4$ ,  $m=0-3$  and  $k+m \leq 4$ ) or

$\text{C}(\text{NR}^5\text{R}^6)(\text{NR}^7\text{R}^8)(\text{NR}^9\text{R}^{10})$ , where

10  $\text{R}^1$  to  $\text{R}^4$   $\text{C}_y\text{F}_{2y+1-z}\text{H}_z$  and

$\text{R}^5$  to  $\text{R}^{10}$  H or  $\text{C}_y\text{F}_{2y+1-z}\text{H}_z$  or

an aromatic heterocyclic cation, in particular a nitrogen- and/or oxygen- and/or sulfur-containing aromatic heterocyclic cation (DE 101 031 89). The process for the preparation of these compounds is characterised in that

15 a)  $\text{BF}_3$ /solvent complexes are reacted 1:1 with alkyllithium with cooling, the majority of the solvent is removed after slow warming, and the solid is subsequently filtered off and washed with a suitable solvent, or

b) lithium salts in a suitable solvent are reacted 1:1 with  $\text{B}(\text{CF}_3)_3$  salts, the mixture is stirred at elevated temperature, the solvent is removed, aprotic non-aqueous solvents, preferably solvents which are used in electrochemical cells, are added to the reaction mixture, and the mixture is dried, or

20 c)  $\text{B}(\text{CF}_3)_3$  salts are reacted 1:1 to 1:1.5 with lithium salts in water at elevated temperature and heated at the boiling point for from 0.5 to 2 hours, the water is removed, aprotic non-aqueous solvents, preferably solvents which are used in electrochemical cells, are added to the reaction mixture, and the mixture is dried.

25 The electrolyte may also comprise fluoroalkylphosphate salts of the general formula

$\text{M}^{n+} ([\text{PF}_x(\text{C}_y\text{F}_{2y+1-z}\text{H}_z)_6-x]^-)_n$

30 in which

$M^{n+}$  is a monovalent, divalent or trivalent cation,

$$1 \leq x \leq 5,$$

$$1 \leq y \leq 8 \text{ and}$$

$0 \leq z \leq 2y + 1$ ,  $n = 1, 2 \text{ or } 3$ , and the ligands  $(C_yF_{2y+1-z}H_z)$  are in each case

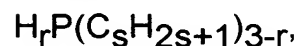
- 5 identical or different, where the fluoroalkylphosphate salts in which  $M^{n+}$  is a lithium cation and the salts

$M^+([PF_4(CF_3)_2]^-)$ , where  $M^+ = Cs^+, Ag^+ \text{ or } K^+$ ,

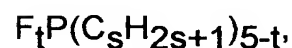
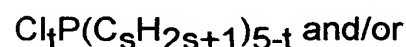
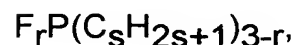
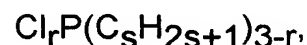
$M^+([PF_4(C_2F_5)_2]^-)$ , where  $M^+ = Cs^+$ ,

$M^+([PF_3(C_2F_5)_3]^-)$ , where  $M^+ = Cs^+, K^+, Na^+ \text{ or } \text{para-Cl}(C_6H_4)N_2^+$ ,

- 10  $M^+([PF_3(C_3F_7)_3]^-)$ , where  $M^+ = Cs^+, K^+, Na^+, \text{para-Cl}(C_6H_4)N_2^+ \text{ or } \text{para-O}_2N(C_6H_4)N_2^+$  are excluded (DE 100 558 12). The process for the preparation of these fluoroalkylphosphate salts is characterised in that at least one compound of the general formula



- 15  $OP(C_sH_{2s+1})_3,$



- 20 in which in each case

$$0 \leq r \leq 2$$

$$3 \leq s \leq 8 \text{ and}$$

$$0 \leq t \leq 4,$$

- is fluorinated by electrolysis in hydrogen fluoride, the resultant mixture of fluorination products is separated, and the resultant fluorinated alkylphosphorane is reacted with a compound of the general formula  $M^{n+}(F^-)_n$ , in which  $M^{n+}$  and  $n$  are as defined above, in an aprotic solvent or solvent mixture with exclusion
- 25

of moisture, and the resultant fluoroalkylphosphate salt is purified and isolated by conventional methods.

The compounds according to the invention can be employed in electrolytes for electrochemical cells containing positive-electrode material consisting of

5 coated metal cores selected from the group consisting of Sb, Bi, Cd, In, Pb, Ga and tin or alloys thereof (DE 100 16 024). The process for the preparation of this positive-electrode material is characterised in that

a) a suspension or sol of the metal or alloy core in urotropin is prepared,

b) the suspension are emulsified with C<sub>5</sub>-C<sub>12</sub>-hydrocarbons,

10 c) the emulsion are precipitated onto the metal or alloy cores, and

d) the metal hydroxides or oxyhydroxides are converted into the corresponding oxide by heating the system.

The compounds according to the invention can also be employed in electrolytes for electrochemical cells having negative electrodes made from common

15 lithium intercalation and insertion compounds, but also with negative-electrode materials consisting of lithium mixed oxide particles coated with one or more metal oxides (DE 199 22 522). They may also consist of lithium mixed oxide particles which are coated with one or more polymers (DE 199 46 066), obtained by a process in which the particles are suspended in a solvent, and the

20 coated particles are subsequently filtered off, dried and optionally calcined.

The compounds according to the invention can likewise be employed in systems having negative electrodes consisting of lithium mixed oxide particles with one or more coatings of alkali metal compounds and metal oxides (DE 100 14 884). The process for the preparation of these materials is charac-

25 terised in that the particles are suspended in an organic solvent, an alkali metal salt compound suspended in an organic solvent is added, metal oxides dissolved in an organic solvent are added, a hydrolysis solution is added to the suspension, and the coated particles are subsequently filtered off, dried and calcined. The compounds according to the invention can likewise be employed

30 in systems comprising positive-electrode materials with doped tin oxide (DE 100 257 61). This positive-electrode material is prepared by

- a) adding urea to a tin chloride solution,
- b) adding urotropin and a suitable doping compound to the solution,
- c) emulsifying the resultant sol in petroleum ether,
- d) washing the resultant gel and removing the solvent by suction, and
- 5 e) drying and heating the gel.

The compounds according to the invention can likewise be employed in systems comprising positive-electrode materials with reduced tin oxide (DE 100 257 62). This positive-electrode material is prepared by

- a) adding urea to a tin chloride solution,
- 10 b) adding urotropin to the solution,
- c) emulsifying the resultant sol in petroleum ether,
- d) washing the resultant gel and removing the solvent by suction,
- e) drying and heating the gel, and
- f) exposing the resultant  $\text{SnO}_2$  to a reducing gas stream in an aeratable oven.

15

The invention is explained below with reference to examples. These examples serve merely to explain the invention and do not restrict the general inventive thinking.

## 20 **Examples**

### Example 1:

Synthesis of dilithium perfluoro-1,2-bis(diethyltrifluorophosphato)ethane

25

9.50 g of a solvent mixture (ethylene carbonate : dimethyl carbonate : diethyl carbonate = 2 : 2 : 1 ratio by weight) and 3.50 g (4.9 mmol) of perfluoro-1,2-bis(diethyldifluorophosphorano)ethane were added at room temperature to 0.44 g (16.9 mmol) of LiF in a PFA vessel under a dry gas atmosphere. The  
30 reaction mixture was stirred at room temperature for three hours until all the perfluoro-1,2-bis(diethyldifluorophosphorano)ethane (base sediment) had dis-

solved. The excess LiF was filtered off, and the solution (electrolyte), which comprised 3.75 g of dilithium perfluoro-1,2-bis(diethyltrifluorophosphato)ethane (corresponding to a salt concentration in the electrolyte solution of 28.3% or 0.48 mol/l), was analysed by  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra. To this end, the spectra were measured for clean electrolytes in an FEP tube without dilution with another solvent using a special method ( $\text{CD}_3\text{COCD}_3$  film).  $\text{CCl}_3\text{F}$  was used as external reference in the film. The frequency of 566.22 Hz of 85%  $\text{H}_3\text{PO}_4$  as  $^{31}\text{P}$  reference in acetone- $\text{d}_6$  was separately determined experimentally. Both  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra were measured using a Bruker DRX 500 spectrometer (470.6 MHz for  $^{19}\text{F}$  and 202.5 Mhz for  $^{31}\text{P}$ ).

The  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra show the formation of different stereoisomers of the salt dilithium perfluoro-1,2-bis(diethyltrifluorophosphato)ethane through the reaction of the fluoride ion with the phosphorus atom between perfluoroethyl groups or between perfluoroethyl group and perfluoroethylene bridge in the starting molecule perfluoro-1,2-bis(diethyldifluorophosphorano)ethane.



Isomer A (about 67%)

$^{19}\text{F}$  NMR: -46.19 dm (2 F, 2 PF); -87.57 dm (4 F, 2  $\text{PF}_2$ ); -82.28 m (6 F, 2  $\text{CF}_3$ ); -82.42 m (6 F, 2  $\text{CF}_3$ ); -112.00 dm (4 F, 2  $\text{CF}_2$ ); -115.13 dm (4 F, 2  $\text{CF}_2$ ); -116.25 dm (4 F, 2  $\text{CF}_2$ );  $J^1_{\text{P,F}} = 927 \text{ Hz}$ ;  $J^1_{\text{P,F}} = 922 \text{ Hz}$ ;  $J^2_{\text{P,F}} = 105 \text{ Hz}$ ;  $J^2_{\text{P,F}} = 74 \text{ Hz}$ ;  $J^2_{\text{P,F}} = 77 \text{ Hz}$ .

$^{31}\text{P}$  NMR: -144.7 qm

Isomer B (about 33%)

$^{19}\text{F}$  NMR: -43.39 dm (2 F, 2 PF); -87.73 dm (4 F, 2  $\text{PF}_2$ ); -80.39 m (12 F, 4  $\text{CF}_3$ ); -110.55 dm (4 F, 2  $\text{CF}_2$ ); -115.70 dm (8 F, 4  $\text{CF}_2$ );

$$J_{P,F}^1 = 860 \text{ Hz}; J_{P,F}^1 = 930 \text{ Hz.}$$

<sup>31</sup>P NMR: -144.8 qm

Example 2:

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Synthesis of a mixture of dilithium perfluoro-1,2-bis(diethyltrifluorophosphato)-ethane and lithium tris(pentafluoroethyl)trifluorophosphate

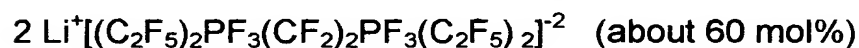
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9.27 g of a solvent mixture (ethylene carbonate : dimethyl carbonate : diethyl carbonate = 2 : 2 : 1 ratio by weight) and 3.39 g of a mixture of perfluoro-1,2-bis(diethyldifluorophosphorano)ethane (about 60 mol%) and tris(pentafluoroethyl)difluorophosphorane (about 40 mol%) [this mixture was prepared by electrochemical fluorination of 1,2-bis(diethylphosphino)ethane and used further without separation] were added at room temperature to 0.46 g

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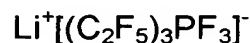
(17.7 mmol) of LiF in a PFA vessel under a dry gas atmosphere. The reaction mixture was stirred at room temperature for three hours until all the perfluorinated starting material (base sediment) had dissolved. The excess LiF was filtered off, and the solution (electrolyte), which comprised 2.60 g of dilithium perfluoro-1,2-bis(diethyltrifluorophosphato)ethane (corresponding to a salt concentration in the electrolyte solution of 0.34 mol/l) and 1.02 g of lithium tris(pentafluoroethyl)trifluorophosphate (corresponding to a salt concentration in the electrolyte solution of 0.23 mol/l), was analysed by <sup>19</sup>F and <sup>31</sup>P NMR spectra. The total concentration of the salt in the electrolyte solution was 28.1%. To this end, the spectra were measured as described under Example 1 and confirm the presence of the two salts in the solution.

25



<sup>31</sup>P NMR: -144.7 qm

30



$^{31}\text{P}$  NMR: -150.3 qm

Example 3:

5    Synthesis of di(tetraethylammonium)perfluoro-1,2-bis(diethyltrifluorophosphato)ethane

10    The synthesis of di(tetraethylammonium)perfluoro-1,2-bis(diethyltrifluorophosphato)ethane was carried out analogously to the synthesis described in Example 1, with anhydrous tetraethylammonium fluoride being used instead of LiF.

●     $^{19}\text{F}$  and  $^{31}\text{P}$  NMR spectra analyses show exclusively signals which can be assigned to the anion (see Example 1).

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Example 4

Oxidation stability of the perfluoro-1,2-bis(diethyltrifluorophosphato)ethane anion

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●    In a measurement cell with platinum working electrode, lithium counter-electrode and lithium reference electrode, in each case 5 cyclic voltammograms were recorded one after the other. To this end, the potential was firstly increased starting from the rest potential at a rate of 10 mV/s to 6 V against Li/Li<sup>+</sup>, and then moved back to the rest potential.

25

Electrolyte: 0.5 mol/kgLm of dilithium perfluoro-1,2-bis(diethyltrifluorophosphato)ethane in EC/DMC (1:1, ethylene carbonate/dimethyl carbonate). The oxidation potential was determined as > 5 V against Li/Li<sup>+</sup> (in this respect, see Figure 1).

30



## Drawings

Figure 1

- 5 Figure 1 shows the results from the measurement cell described in Example 4, with the cyclic voltammograms being recorded under the conditions quoted in this example with dilithium perfluoro-1,2-bis(diethyltrifluorophosphato)ethane as conductive salt.

## PATENT CLAIMS

1. Fluoroalkylphosphate salts of the general formula



(I)

in which

10  $M^{a+}$  a monovalent, divalent or trivalent cation,

$a = 1, 2$  or  $3$ ,

$b = 2$  for  $a = 1$ ,

15  $b = 2$  for  $a = 3$ ,

$b = 1$  for  $a = 2$

and in each case

20  $1 \leq n \leq 8$ ,

$0 \leq m \leq 2$  for  $n = 1$  or  $2$ ,

$0 \leq m \leq 4$  for  $3 \leq n \leq 8$ ,

25  $1 \leq x \leq 12$ ,

$0 \leq y \leq 2$ ,

where  $R_1$  and  $R_2$  are in each case identical or different and are selected from the group consisting of fluorine, hydrogen, alkyl, fluoroalkyl and per-fluoroalkyl substituents, and

5 where the substituents ( $C_nF_{2n+1-m}H_m$ ) are in each case identical or different.

2. Fluoroalkylphosphate salts according to Claim 1, characterised in that the cation  $M^{a+}$  is an alkali metal cation, preferably a lithium, sodium or  
10 potassium cation, particularly preferably a lithium cation.

3. Fluoroalkylphosphate salts according to Claim 1, characterised in that the cation  $M^{a+}$  is a magnesium or aluminium cation.

15 4. Fluoroalkylphosphate salts according to Claim 1, characterised in that  $M^{a+}$  is an organic cation, preferably

a nitrosyl cation, a nitryl cation or an organic cation with the general formula  $[N(R^7)_4]^+$ ,  $[P(R^7)_4]^+$ ,  $[P(N(R^7)_2)_4]^+$  or  $[C(N(R^7)_2)_3]^+$ , where the  
20 radicals  $R^7$  are in each case identical or different and stand for

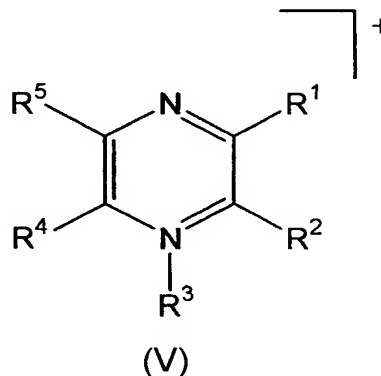
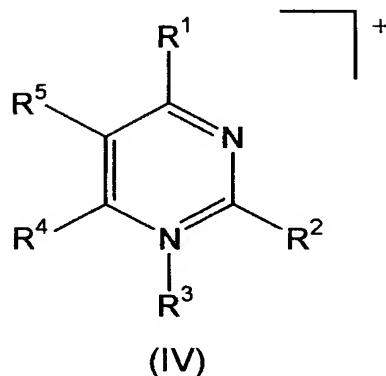
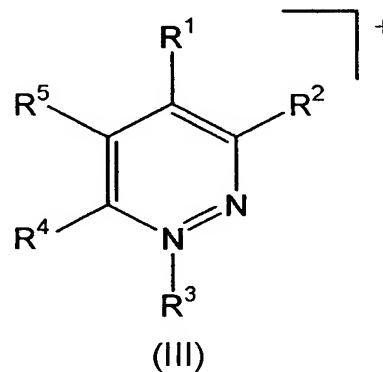
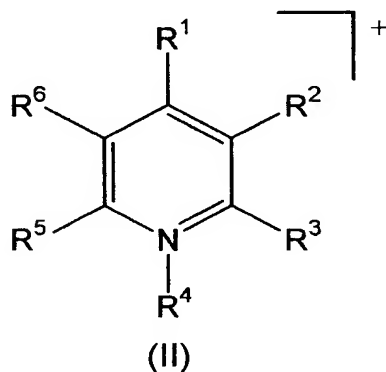
H or alkyl ( $C_{1-10}$ ),

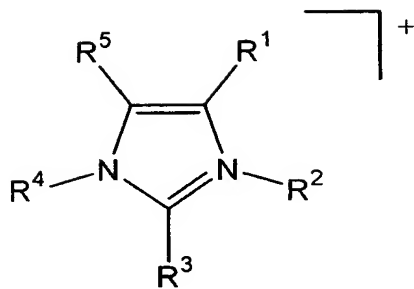
25 where any H atoms in the alkyl chain may be substituted by fluorine or an aromatic radical, optionally containing heteroatoms, or a cycloalkyl radical, preferably having 5-6 members, and/or C atoms in the alkyl chain may be replaced by heteroatoms, preferably oxygen.

5. Fluoroalkylphosphate salts according to Claim 4, characterised in that  
30  $1 \leq o \leq 6$ ,  $1 \leq p \leq 2o+1$ ,  $1 \leq q \leq 2o+1$  and A in each case denotes an

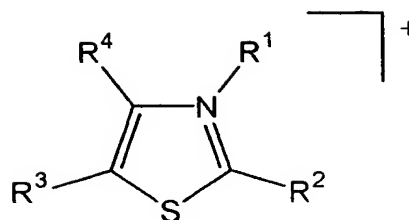
aromatic radical, which optionally contains heteroatoms, or a cycloalkyl radical, which preferably has 5 or 6 members.

6. Fluoroalkylphosphate salts according to Claim 4 or 5, characterised in that
- 5 A in each case denotes a 5- or 6-membered aromatic radical, which optionally contains nitrogen and/or sulfur and/or oxygen atoms, or a cycloalkyl radical, which preferably has 5 or 6 members, preferably a phenyl radical or pyridine radical.
- 10 7. Fluoroalkylphosphate salts according to Claim 1, characterised in that  $M^{a+}$  is a heteroaromatic cation of the general formula (II) to (IX)

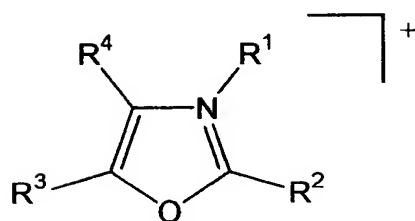




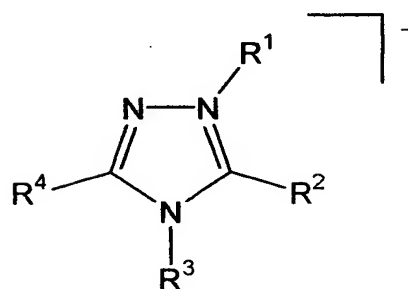
(VI)



(VII)



(VIII)



(IX)

in which the radicals  $R^1$  to  $R^6$  are in each case identical or different, and if desired also two of the radicals  $R^1$  to  $R^6$  together, denote an H radical, a halogen radical, preferably a fluorine radical, or a  $C_{1-8}$ -alkyl radical, which may optionally be substituted by

F, Cl,  $N(C_rF_{(2r+1-s)}H_s)_2$ ,  $O(C_rF_{(2r+1-s)}H_s)$ ,  $SO_2(C_rF_{(2r+1-s)}H_s)$  or  $C_rF_{(2r+1-s)}H_s$ , in which  $1 \leq r \leq 6$  and  $0 \leq s \leq 2r+1$ ,

where the radicals  $R^1$  to  $R^6$  cannot be halogens if the radicals  $R^1$  to  $R^6$  are bonded directly to nitrogen.

8. Fluoroalkylphosphate salts according to one of Claims 1 to 7, characterised in that  $1 \leq n \leq 6$ , preferably  $1 \leq n \leq 3$ .

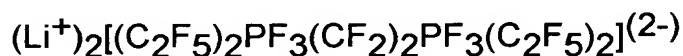
9. Fluoroalkylphosphate salts according to one of Claims 1 to 8, characterised in that  $1 \leq x \leq 8$ , preferably  $1 \leq x \leq 4$ .

10. Fluoroalkylphosphate salts according to one of Claims 1 to 9, characterised in that  $m = 0$ .

11. Fluoroalkylphosphate salts according to one of Claims 1 to 10, characterised in that  $y = 2$ .

12. Fluoroalkylphosphate salts according to one of Claims 1 to 11, characterised in that  $R_1$  and  $R_2$  are fluorine.

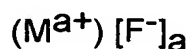
13. Fluoroalkylphosphate salts according to Claim 1:



and



14. Process for the preparation of fluoroalkylphosphate salts according to one of Claims 1 to 13, characterised in that at least one fluoro- $\alpha,\omega$ -bis(alkyl-fluorophosphorano)alkane is reacted with at least one fluoride salt of the general formula (X)



(X)

in which  $(\text{M}^{a+})$  and has the meaning according to Claims 1 to 13, in solution to give a fluoroalkylphosphate salt of the general formula (I) according

to Claim 1, and the latter is, where appropriate, purified and/or isolated by conventional methods.

15. Process according to Claim 14, characterised in that the fluoro- $\alpha,\omega$ -bis-  
(alkylfluorophosphorano)alkane employed is at least one compound of  
the general formula (XI)



(XI)

in which

$1 \leq n \leq 8$ ,  $0 \leq m \leq 2$  for  $n = 1$  or  $2$ ,  $0 \leq m \leq 4$  for  $3 \leq n \leq 8$ ,  $1 \leq x \leq 12$ ,

$0 \leq y \leq 2$ ,

where  $\text{R}_1$  and  $\text{R}_2$  are identical or different and are selected from the group consisting of fluorine, hydrogen, alkyl, fluoroalkyl and perfluoroalkyl substituents, and

where the substituents  $(\text{C}_n\text{F}_{2n+1-m}\text{H}_m)$  are in each case identical or different.

16. Process according to Claim 14 or 15, characterised in that the compound of the general formula (X) according to Claim 14 is employed in an excess of up to 10 fold, preferably up to 5 fold, particularly preferably up to 2 fold, based on the amount of fluoro- $\alpha,\omega$ -bis(alkylfluorophosphorano)-alkane(s).

17. Process according to one of Claims 14 to 16, characterised in that the reaction with the compound of the general formula (X) according to Claim

14 is carried out at a temperature of from -35 to +80°C, preferably from -20 to +50°C, particularly preferably from -10 to 25°C.

18. Process according to one of Claims 14 to 17, characterised in that the sol-  
5 vents employed are organic carbonates, preferably ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate or methyl propyl carbonate, organic esters, preferably methyl formate, ethyl formate, methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, methyl butyrate, ethyl  
10 butyrate,  $\gamma$ -butyrolactone, organic ethers, preferably diethyl ether, di-methoxyethane, diethoxyethane, organic amides, preferably dimethyl-formamide or dimethylacetamide, sulfur-containing solvents, preferably dimethyl sulfoxide, dimethyl sulfide, diethyl sulfide or propane sulfone, aprotic solvents, preferably acetonitrile, acrylonitrile, propionitrile or ace-  
15 tone, or at least partially fluorinated derivatives of the above-mentioned solvents, or mixtures of at least two of these solvents and/or fluorinated derivatives of these solvents.

19. Mixture comprising

- 20 a) at least one fluoroalkylphosphate salt of the general formula (I) according to Claims 1 to 13

and

- 25 b) at least one polymer.

20. Mixture according to Claim 19, characterised in that it comprises from 5 to  
30 90% by weight of component a) and from 95 to 5% by weight of component b), preferably from 10 to 80% by weight of component a) and from



90 to 20% by weight of component b), in each case based on the sum of components a) and b).

21. Mixture according to Claim 19 or 20, characterised in that component b) is a homopolymer or copolymer of acrylonitrile, vinylidene difluoride, methyl methacrylate, tetrahydrofuran, ethylene oxide, siloxane, phosphazene or a mixture of at least two of the above-mentioned homopolymers and/or copolymers.
22. Mixture according to Claim 21, characterised in that component b) is a homopolymer or copolymer of vinylidene difluoride, acrylonitrile, methyl methacrylate, tetrahydrofuran, preferably a homopolymer or copolymer of vinylidene difluoride.
23. Mixture according to one of Claims 19 to 22, characterised in that the polymer is at least partially crosslinked.
24. Mixture according to one of Claims 19 to 23, characterised in that it additionally comprises at least one solvent.
25. Mixture according to Claim 24, characterised in that the solvents present are organic carbonates, preferably ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate or methyl propyl carbonate, organic esters, preferably methyl formate, ethyl formate, methyl acetate, ethyl acetate, methyl propionate, ethyl propionate, methyl butyrate, ethyl butyrate,  $\gamma$ -butyrolactone, organic ethers, preferably diethyl ether, dimethoxyethane, diethoxyethane, organic amides, preferably dimethylformamide or dimethylacetamide, sulfur-containing solvents, preferably dimethyl sulfoxide, dimethyl sulfide, diethyl sulfide or propane sulfone, aprotic solvents, preferably acetonitrile, acrylonitrile or acetone, or at least partially fluorinated deriva-

tives of the above-mentioned solvents, or mixtures of at least two of these solvents and/or fluorinated derivatives of these solvents.

- 5 26. Use of at least one fluoroalkylphosphate salt according to one of Claims 1 to 13 or at least one mixture according to one of Claims 19 to 25 in electrolytes, primary batteries, secondary batteries, capacitors, supercapacitors or galvanic cells, if desired also in combination with further conductive salts and/or additives.
- 10 27. Electrolytes comprising at least one fluoroalkylphosphate salt according to one of Claims 1 to 13 or at least one mixture according to one of Claims 19 to 25.
- 15 28. Electrolytes according to Claim 27, characterised in that the concentration of the fluoroalkylphosphate salt(s) in the electrolyte is from 0.01 to 3 mol/l, preferably from 0.01 to 2 mol/l, particularly preferably from 0.1 to 1.5 mol/l.
- 20 29. Primary batteries containing at least one fluoroalkylphosphate salt according to one of Claims 1 to 13 or at least one mixture according to one of Claims 19 to 25.
- 25 30. Secondary batteries containing at least one fluoroalkylphosphate salt according to one of Claims 1 to 13 or at least one mixture according to one of Claims 19 to 25.
- 30 31. Capacitors containing at least one fluoroalkylphosphate salt according to one of Claims 1 to 13 or at least one mixture according to one of Claims 19 to 25.

32. Supercapacitors containing at least one fluoroalkylphosphate salts according to one of Claims 1 to 13 or at least one mixture according to one of Claims 19 to 25.
- 5 33. Galvanic cells containing at least one fluoroalkylphosphate salt according to one of Claims 1 to 13 or at least one mixture according to one of Claims 19 to 25.

### **A b s t r a c t**

- 5    The present invention relates to fluoroalkylphosphate salts and to a process for their preparation. The present invention furthermore relates to mixtures which comprise the fluoroalkylphosphate salts according to the invention, and to the use of these salts or these mixtures in electrolytes, primary batteries, secondary batteries, capacitors, supercapacitors or galvanic cells.

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